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# Capacitive Deionization of Saline Water by Using MoS<sub>2</sub>-Graphene Hybrid Electrodes with High Volumetric Adsorption Capacity

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**ABSTRACT:** Capacitive deionization (CDI) has received wide attention as an emerging water treatment technology due to its low energy consumption, low cost and high efficiency. However, the conventional carbon electrode materials for CDI have low densities, which occupy large volumes and are disadvantageous for use in limited space (e.g., in household or on offshore platforms). In order to miniaturize the CDI device, it is quite urgent to develop high volumetric adsorption capacity (VAC) electrode materials. To overcome this issue, we rationally designed and originally developed high VAC MoS<sub>2</sub>-graphene hybrid electrodes for CDI. It is interesting that MoS<sub>2</sub>-graphene hybrid electrode has a much higher NaCl volumetric adsorption capacity of 14.3 mg/cm<sup>3</sup> with a gravimetric adsorption capacity of 19.4 mg/g. It has been demonstrated that the adsorption capacity is significantly enhanced due to the rapid ion transport of MoS<sub>2</sub> and high electrical conductivity of graphene. *In-situ* Raman spectra and high-angle annular dark-field scanning transmission electron microscopy tests demonstrated a favorable Faradaic reaction, which was crucial to enhancing the NaCl volumetric adsorption capacity of MoS<sub>2</sub>-graphene hybrid electrode. This work opens a new avenue for

23 miniaturizing future CDI devices.

## 24 ■ INTRODUCTION

25 With the growth of population and the development of industry, human beings consume a large amount  
26 of fresh water resources.<sup>1</sup> The widespread water scarcity and water contamination problems are  
27 seriously increasing across the world, threatening human health and ecological integrity.<sup>2-5</sup> In coastal  
28 areas, desalination of saline water is an important way to obtain fresh water.<sup>6</sup> Conventional desalination  
29 methods include reverse osmosis thermal distillation and electrodialysis.<sup>7-9</sup> They have demonstrated a  
30 variety of disadvantages in practical applications, such as high energy consumptions and high  
31 economic costs.<sup>10</sup>

32 As an emerging water treatment technology, capacitive deionization (CDI) has gained increasing  
33 attention due to its prominent advantages, such as high efficiency, low cost, low energy consumption  
34 and easy operations and ease of maintenance.<sup>11-13</sup> The principle of CDI is analogous to that of the  
35 electrical double-layer capacitor:<sup>14</sup> When exposed to an external electric field, the charged ions in the  
36 feed water move towards the oppositely charged electrode by electrostatic attraction and are adsorbed  
37 and/or trapped on the surface of electrodes accompanied by simultaneous energy storage, thus the  
38 deionized water is produced in the outlet. When the electric field is reversed or the electrodes were  
39 short-circuited, the ions adsorbed in the electrodes are released, accompanied by the release of energy  
40 stored in the electrodes, therefore the electrodes are regenerated. Various CDI models and techniques,  
41 such as flow electrode capacitive deionization, membrane capacitive deionization, faradaic CDI and  
42 hybrid CDI have attracted increasing attention in the last decade.<sup>9,15-17</sup>

43 Electrode materials are vital for the CDI performance. Key features of an excellent electrode  
44 material include high electrical conductivity, high adsorption capacity, reasonable pore structure, high

45 chemical and mechanical stability, environmentally friendly, and favorable water wettability.<sup>18</sup>  
46 Traditional electrode materials used in CDI, including activated carbon (AC), porous carbon, carbon  
47 fibers, carbon cloths, carbon nanotubes and graphene have been extensively studied due to their high  
48 chemical stability, high electrical conductivity and high adsorption capacity.<sup>19</sup> In recent years, some  
49 materials with pseudocapacitance such as TiO<sub>2</sub>, MnO<sub>2</sub>, MoS<sub>2</sub>, some molybdate and phosphate  
50 attracted a lot of attentions.<sup>20-22</sup> Despite great efforts have been devoted to preparing novel CDI  
51 electrode materials,<sup>23-25</sup> most of current studies are focused on the enhancement of the gravimetric  
52 adsorption capacity (GAC, mg/g) while little attention has been paid to the enhancement of the  
53 volumetric adsorption capacity (VAC, mg/cm<sup>3</sup>). Traditional carbonaceous electrodes are relatively low  
54 in density, such as only 0.4-0.6 g/cm<sup>3</sup> for activated carbon and 1-2 g/cm<sup>3</sup> for multiwall carbon  
55 nanotubes.<sup>26</sup> The utilization of low density materials leads to its low VAC, which is unfavorable when  
56 the CDI devices are used in a limited space (e.g., in household or on offshore oil/gas platforms).<sup>27</sup>  
57 Therefore, enhancing the VAC of the CDI electrodes is a major objective for future CDI development.

58 MoS<sub>2</sub> is one of the most interesting two-dimensional layered materials, in which two layers of sulfur  
59 atoms are sandwiched by a layer of molybdenum atoms. Each three-layer structure is connected by a  
60 weak Van Der Waals force, which gives MoS<sub>2</sub> a variety of fascinating properties such as large surface  
61 area, high density and fast ionic conductivity.<sup>28</sup> Specifically, the density of MoS<sub>2</sub> is around 4-5 g/cm<sup>3</sup>,  
62 which is much higher than that of carbon materials.<sup>29</sup> Combining the high electrical conductivity of  
63 graphene with the high density of MoS<sub>2</sub> may result in a highly conductive and compact electrode  
64 material for CDI.

65 Herein, we rationally designed and originally developed a novel hybrid MoS<sub>2</sub>-graphene electrode  
66 for CDI applications (Figure 1a and 1b). The MoS<sub>2</sub>-graphene electrode showed a high NaCl adsorption

67 capacity ( $VAC_{NaCl}$ ) as well as a high NaCl adsorption capacity ( $GAC_{NaCl}$ ), as a result of the high  
68 electrical conductivity of graphene and the rapid ion transport of  $MoS_2$ . This study reveals a new  
69 avenue for miniaturizing future CDI devices.

## 70 ■ EXPERIMENT

71 **Preparation.** Graphene oxide (GO, 99.5%, Graphene-king Company, Shanghai, China), ammonium  
72 molybdate tetrahydrate ( $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ) and thiourea were purchased from Aladdin (Shanghai,  
73 China). All the chemicals were analytically pure and not purified further.  $MoS_2$ -graphene hybrid  
74 electrodes were synthesized through a simple *in-situ* growth strategy (Figure 1b). Typically, 1.12 g  
75 thiourea and 40 mg graphene oxide (dispersed in DI water, 2 mg/mL) were dissolved in 75 mL water  
76 under vigorous stirring to make a homogenous mixture. Then 4 g  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  was added into  
77 the mixture under stirring for 30 min followed by transferring into the 100 mL Teflon-lined stainless  
78 autoclave and hydrothermally treated at 170 °C for 12 h. Afterward, the sediment was separated by  
79 suction filtration and washed by absolute ethanol and DI water followed by drying at 60 °C at ambient  
80 air. At last, the resultant powder was calcined at 600 °C with a ramping rate of 5 °C /min under a  
81 flowing argon atmosphere. Samples with graphene oxide additive amount of 0, 40, 60, 80, 100 and  
82 200 mg were named by  $MoS_2$ , MG-0.8, MG-1.2, MG-1.6, MG-1.9 and MG-3.8, respectively.

83 **Characterization.** Scanning electron microscope (SEM, Hitachi S-4800) and transmission  
84 electron microscope (TEM, JEM 2100) were used to observe the morphological and structural  
85 properties of the samples. The phase compositions were determined using the X-ray diffractometer  
86 (XRD, Cu  $K\alpha$ , 40 kV, 20 mA). Raman spectroscopy were investigated by a spectrometer with a 633  
87 nm  $Ar^+$  laser and *in-situ* Raman spectra of whole cyclic voltammetry (CV) cycle between 0.5 V and -  
88 0.5 V were conducted on a Raman spectrometer (HORIBA scientific, LabRAM HR Evolution, France)

with a 633 nm laser. Nitrogen isothermal adsorption-desorption curves were investigated (Autosorb-IQ2, America). The specific surface area and the pore size distribution were determined by the Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) and density Functional Theory (DFT) model, respectively. Water wettability was evaluated by drop shape analysis using Kruss, DSA100 instrument. Electrochemical performance was evaluated through an electrochemical workstation (CHI 660D, Chenhua, Shanghai). The working electrode was fabricated through mixing of polytetrafluoroethylene (PTFE) aqueous dispersion and active material with a ratio of 1: 9 in weight and shaped into 1 cm square film. The CV and galvanostatic charge-discharge (GCD) curves and electrochemical impedance spectroscopy (EIS) were measured in a 0.5 M NaCl solution with a three-electrode system. The calomel electrode and graphite film serve as reference electrode and counter electrode, respectively. The capacitance is calculated by the equation (1)

$$C = \frac{\int I dV}{2mv\Delta V} \quad (1)$$

Where  $C$  is the capacitance (F/g),  $I$  is the response current density (A),  $m$  is the mass of active material (g),  $v$  is the scanning rate (V/s), and  $\Delta V$  is the applied voltage window during the cyclic voltammetry test (V). The proportion of contribution of capacitive charge and the diffusion-controlled charge were calculated according to the equation (2).<sup>30</sup>

$$i(V) = k_1 v + k_2 v^{0.5} \quad (2)$$

Where the  $i$  is the current (A), the  $v$  is the scanning rate (mV/s),  $k_1$  and  $k_2$  are constant values at a fixed potential.  $k_1 v$  is related to the capacitive current raised from electrical double layer (EDL) and  $k_2 v^{0.5}$  is related to diffusion-controlled charge.

**Batch-Mode CDI Experiments.** The electrode for batch-mode CDI experiments was fabricated through adequate mixing of the PTFE, conductive carbon black and as-prepared active

material with a ratio of 1:1:8 in weight, then was shaped into 65 mm square film and casted onto the graphite film current collector. An asymmetric electrode system was assembled using as-prepared electrode and graphite film (GF) as the working electrode and the counter electrode (GF||MG-1.6 electrode pairs), respectively. The other asymmetric electrode was assembled using as-prepared electrode and graphite film loaded with activated carbon as the working electrode and the counter electrode (AC||MG-1.6 electrode pairs), respectively. The homemade device (Figure 1a) was used to examine the salt adsorption performance as demonstrated in previous work by our group.<sup>31,12</sup> The two CDI electrodes was separated by placing a spacer between them. A 50 mL NaCl solution was driven cyclically through the electrodes via a peristaltic pump. A conductivity meter (SevenMulti, METTLER TOLEDO, America) was used to monitor the conductivity of the NaCl solution online. When it is necessary to compare the variations of solution conductivity in different batch-mode test, the initial solution conductivity is normalized just for comparative purposes to eliminate the system error. In this work, graphite film loaded with as-prepared material was used as cathode, graphite film or graphite film loaded with activated carbon was used as anode. The GAC was calculated in theory by the equation (3):

$$GAC = GAC_T - GAC_{NA} \quad (3)$$

Where the  $GAC$  is gravimetric adsorption capacity (mg/g), the  $GAC_T$  is the total  $GAC$  obtained by CDI tests of the whole electrodes (mg/g), the  $GAC_{NA}$  is the premeasured  $GAC$  of non-active materials (mg/g). For CDI test with GF||MG-1.6 electrode pairs,  $Na^+$  ions gravimetric adsorption capacity ( $GAC_{Na}$ ) was used to evaluate the ability of deionization of active materials, which was calculated by the equation (4) as follow.

$$GAC_{Na} = \frac{0.394(C_{NA} - C_T)V}{M} \quad (4)$$

Where 0.394 is the mass fraction of sodium in NaCl,  $C_{Na}$  is the NaCl aqueous solution concentration during the desalination test of non-active material (mg/L) (Figure S1),  $C_T$  is the NaCl aqueous solution concentration during the desalination test of the as-prepared electrodes (mg/L),  $M$  is the quality of as-prepared electrode material (g) and  $V$  is volume of NaCl solution (L). The thickness of active material film is calculated by follow equation (5):

$$T_{af} = T_t - T_{cc} \quad (5)$$

Where  $T_{af}$  is active material film thickness ( $\mu\text{m}$ ),  $T_t$  is average total thickness ( $\mu\text{m}$ ),  $T_{cc}$  is average current collector (graphite film) thickness ( $\mu\text{m}$ ). Both the  $T_{cc}$  and  $T_t$  are measured by micrometer (Figure S3). The  $\text{Na}^+$  volumetric adsorption capacity ( $VAC_{Na}$ ) was calculated by the equation (6):

$$VAC_{Na} = \frac{GAC_{Na} \times M}{T_{af} \times a} \quad (6)$$

Where  $a$  is the area of active electrode film on the current collector ( $\text{cm}^2$ ), respectively. For the CDI test with ACIMG-1.6 electrode pairs, the  $GAC_{NaCl}$  was calculated by the equation (7) as follow.

$$GAC_{NaCl} = \frac{(C_{Na} - C_T)V}{m_t} \quad (7)$$

Where  $m_t$  is the quality of total mass both cathode and anode electrode material (g). The NaCl  $VAC_{NaCl}$  was calculated by the equation (8):

$$VAC_{NaCl} = \frac{GAC_{NaCl} \times m_t}{aT_{af} + bT_{AC}} \quad (8)$$

Where  $b$  is activated carbon film area ( $\text{cm}^2$ ),  $T_{AC}$  is activated carbon film thickness (cm). The  $T_{AC}$  was calculated adopted similar method with  $T_{af}$ . Average  $\text{Na}^+$  adsorption rate ( $ASAR_{Na}$ ) ( $\text{mg}/\text{cm}^3/\text{min}$ ) was calculated by equation (9):

$$ASAR_{Na} = \frac{0.394V \int_0^t (C_{Na}(t) - C_T(t))dt}{T_{af} \times a \times t} \quad (9)$$

Where  $C_{Na}(t)$  and  $C_T(t)$  is instant concentration of the NaCl aqueous solution during the deionization (mg/L),  $t$  is the time of deionization (min). During the regeneration of the electrode, the external



direct voltage was removed and the work electrode was directly connected with the counter electrode by a copper wire.

The regeneration tests were conducted at a flow rate of 60 mL/min and a direct voltage of 1.2 V. The initial conductivity of the NaCl solution was 200  $\mu\text{S}/\text{cm}$ . When the electrodes were regenerated, they were connected by wire directly to release the adsorbed ions.

## ■ RESULTS AND DISCUSSION

**Structure and Composition Analysis.** The morphologies of the obtained materials were demonstrated by TEM and SEM images. Figure 1c-d show the SEM images of the MG-1.6. There are a large number of  $\text{MoS}_2$  pleats on the surface of the particles and these protrusions are uniform and interlaced in a flaky shape, which is advantageous for increasing the specific surface area. According to the TEM (Figure 1e-1f) and HRTEM (Figure 1g) images of MG-1.6, it can be clearly observed that a large number of  $\text{MoS}_2$  sheets are homogenously distributed on the surface of the graphene, which is conducive to increase the conductivity of electrode. The lattice spacing was calculated to be 0.68 nm (Figure 1g), corresponding to the (002) lattice plane of the hexagonal  $\text{MoS}_2$ .<sup>32</sup> The thickness of the  $\text{MoS}_2$  layer of MG-1.6 is calculated to be 9 nm corresponding to layers number of 14, which contributes to increase conductivity of the  $\text{MoS}_2$ -graphene hybrid electrode. It was found that as the additive amount of graphene oxide increases, the agglomeration of the sheet-like  $\text{MoS}_2$  on graphene is alleviated and the sheet becomes smaller with a better dispersion (Figure S2). When the additive amount of graphene oxide is more than 1.9 wt%, the  $\text{MoS}_2$  sheets cannot be clearly distinguished (Figure S2f). This result is possibly due to the fact that graphene provides nucleation sites for the formation of  $\text{MoS}_2$ ,<sup>33,34</sup> and an increase in the amount of graphene makes the nucleation rate surpass the growth rate, resulting in a reduction in the size of  $\text{MoS}_2$  sheets. However, too small  $\text{MoS}_2$  crystals

are not beneficial to preventing graphene stacking. Conversely, the highly agglomerated MoS<sub>2</sub> is unfavorable for mass transfer, because the number of adsorption sites is limited.

The phase properties of different samples were examined by XRD (Figure 2a). The obvious diffraction peaks located at 13.7°, 33.6° and 59.9° correspond to the (002), (100) and (008) planes of hexagonal MoS<sub>2</sub> (JCPDS, No. 37-1492), respectively, indicating good crystalline nature of MoS<sub>2</sub>. That is favorable to the chemical stability of electrode. Actually, the peaks located at 26°, 37.0° and 53.5° in the Figure 2a are corresponding to (011), (020) and (022) planes of MoO<sub>2</sub> (JCPDS 65-5787).<sup>35</sup> MoO<sub>2</sub> is produced because the (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O is excessive and the thiourea is insufficient. The excessive molybdate ions were transformed into MoO<sub>2</sub>. As the electrical resistivity of MoO<sub>2</sub> (10<sup>-5</sup> Ω cm<sup>-1</sup>) is much lower than that of MoS<sub>2</sub> (~1 Ω cm<sup>-1</sup>), therefore MoO<sub>2</sub> is beneficial for conductivity of the as-prepared materials.<sup>36,37</sup>

The specific surface areas calculated from N<sub>2</sub> adsorption-desorption isotherms (left of Figure 2b) for MG-0.8, MG-1.2, MG-1.6, MG-1.9, MG-3.8 are 27.2, 28.9, 37.9, 35.3 and 34.2 m<sup>2</sup>/g, respectively. The results implied that the content of graphene affects the specific surface area significantly. Low content of graphene makes MoS<sub>2</sub> agglomerated and excessive graphene makes itself stacked. The hysteresis curves include a hysteresis loop at a high-pressure stage, and the area of the hysteresis loop is related to the pore volume.<sup>38</sup> According to the pore size distribution profiles (right of Figure 2b and Figure S4), MG-1.6 has the large portions of mesopores, indicating their superior mass transfer capacities. Moreover, the good hydrophilicity of MG-1.6 has been demonstrated (Figure S5), which favors the CDI process for the practical applications.

The Raman spectra were conducted to examine the structure and topology of the MoS<sub>2</sub>-graphene and the layer number (Figure 2c and 2d). The peaks located at 378 cm<sup>-1</sup> and 405 cm<sup>-1</sup> are corresponding

to  $E_{2g}^1$  and  $A_{1g}$  peaks, respectively.<sup>20</sup>  $E_{2g}^1$  peak is assigned to the in-plane displacement in Mo and S atoms and  $A_{1g}$  is assigned to the out-plane symmetric displacement of S atom along the c-axis.<sup>39</sup> As shown in Figure 2d, a slight blue-shift of  $A_{1g}$  is found, indicating the layer number of  $MoS_2$  decreasing,<sup>40,41</sup> which accounts the effect of inhibition on layer number of  $MoS_2$  by graphene. The peak located at around  $1360\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$  are corresponding to the D and G peaks of graphene (Figure 2c), which arise from the  $sp^3$ -hybridized carbon and the  $sp^2$ -hybridized carbon.<sup>42</sup> The increasing intensity of D and G peaks indicates the increase of graphene content, moreover, the D peak is larger than G peak demonstrating the small degree of graphitization.

**Electrochemical Performance.** The GCD test was implemented to examine the capacitance of the as-prepared samples (Figure 3a). The results show that MG-1.6 has the longest discharge time at  $0.2\text{ A/g}$ , implying that it possesses the largest capacitance among all the electrodes. The sample MG-1.6 was tested at different current densities (Figure S6a). The result shows that it keeps a long discharge time of  $150\text{ s}$  at a large current density of  $1.0\text{ A/g}$ . The extent of IR drop is positively related to the inner electrical resistance of the electrodes.<sup>12,43</sup> The IR drop of MG-1.6 displays the smallest IR drop (the inset of Figure 3a), indicating that it has the smallest inner electrical resistance. The result is due to the preferable distribution of  $MoS_2$  particles of MG-1.6 on the graphene, ensuring a high electrical conductivity and a small internal resistance. The IR drops at different current densities are shown in Figure S6b. The result confirms that the IR drop increases linearly with the increase of current density, which is attributed to the inadequate discharge in the EDL at the onset of discharge. A superior charge-discharge performance and a good cyclic stability of  $10\ 000$  cycles are obtained for MG-1.6 electrode (Figure 3d).

The CV test for exploring the electrochemical behavior in a  $0.5\text{ M NaCl}$  solution shows the

221 rectangular-like closed curve of MG-1.6 (Figure S6c), suggesting good capacitor characteristics.<sup>44</sup> As  
 222 calculated from the area of the rectangular curves, the capacitances of MG-1.6 is 146.1 F/g at a  
 223 scanning rate of 5 mV/s, which is higher than other contrast samples (Figure S6d), implying  
 224 remarkable adsorption capacity. The capacitances of MG-1.6 at different scanning rates are shown in  
 225 Figure S6e. The MG-1.6 still has a capacitance of 47.9 F/g even at a high scan rate of 50 mV/s, which  
 226 is due to the good electrical conductivity of MG-1.6. Two redox peaks at 1 mV/s (Figure S6f)  
 227 demonstrates the existence of a redox process. The proportion of contribution of capacitive charge and  
 228 the diffusion-controlled charge were calculated according to the equation (2). CV curves at 0.2 mV/s  
 229 and 0.5 mV/s have been measured, respectively. Based-on the equation (2), at a given potential  $P$ , two  
 230 known different current values  $i_1$  and  $i_2$  are obtained at two scanning rates  $v_1$  (0.2 mV/s) and  $v_2$  (0.5  
 231 mV/s), thus obtaining a binary equations as follow.

$$232 \quad i_1(P) = 0.2k_1 + \sqrt{0.2}k_2 \quad (10)$$

$$233 \quad i_2(P) = 0.5k_1 + \sqrt{0.5}k_2 \quad (11)$$

234  $k_1$  and  $k_2$  at  $P$  potential can be obtained by solving the above binary equations consisting equation  
 235 (10) and (11). A CV cycle contains a series of potential values, so a series of  $k_1$  and  $k_2$  values can be  
 236 obtained. For the same material,  $k_1$  and  $k_2$  are fixed at a given potential. Therefore, at the scanning rate  
 237 of 0.2 mV/s, the current derived from electric double-layer capacitor can be obtained by the equation  
 238 (12).

$$239 \quad i_{EDLC}(V) = 0.2 \times k_1 \quad (12)$$

240 Where  $i_{EDLC}$  is the current derived from electric double-layer capacitor. These  $i_{EDLC}$  points can be  
 241 linked to form a closed CV curve, which is the shaded part in Figure 3b. The area of shaded part as a  
 242 percentage of the area of the measured CV curve is the percentage of the contribution of the electric

double layer capacitor. The rest is the diffusion-controlled charge contribution. The shadow area is corresponding to the capacitive current at 0.2 mV/s (Figure 3b), which takes a proportion of 72.7%. The result demonstrates that capacitive charge contributes 72.7% of the capacity and the diffusion-controlled charge contributes 27.3% of capacity.

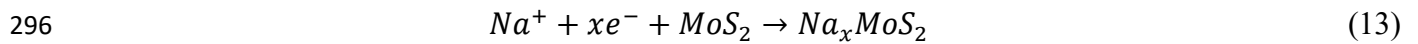
The EIS test for examining the resistance of the as-prepared samples (Figure 3c) shows that each curve has a similar shape which consists of a pressed and rotated semi-circle and a slope line. The pressed and rotated semi-circle is related with the interface resistance between the surface of electrode and the electrolyte bulk. The slope line correlates to the ion diffusion on the surface of electrode.<sup>45,46</sup> It was found that MG-1.6 has relatively small diameter of semicircle, revealing small charge transfer resistance. The result may be attributed to the high conductivity of MG-1.6 arising from the homogenous distribution of MoS<sub>2</sub> particles on the surface of graphene. The slope line correlates with the capacitor characteristics and a greater slope of the line means more capacitor characteristics. The inset of Figure 3c shows a relative larger slope line of MG-1.6, suggesting better capacitor characteristics.

**CDI Performance.** Figure 4a shows the Ragone plots of average salt adsorption rate ( $ASAR_{Na}$ ) versus (*vs.*)  $VAC_{Na}$  of different samples. The result displays that MG-1.6 made the largest decrease of normalized solution conductivity (Figure S8a) and had the largest  $VAC_{Na}$  up to 6.0 mg/cm<sup>3</sup> and it maintained a high salt adsorption rate even at the high  $VAC_{Na}$  stage, which is attributed to the improved microstructure of graphene on MoS<sub>2</sub>. Compared to activated carbon, MG-1.6 can save 54% volume at the same adsorption capacity (Table S1). Figure 4b shows the plots of GAC *vs.* deionization time, and Figure 4c shows the plots of  $VAC_{Na}$  *vs.* deionization time. It is found that  $GAC_{Na}$  of MG-1.6 reached to 8.1 mg/g, and still kept a relatively high deionization rate at the high  $VAC_{Na}$  stage. The high  $GAC_{Na}$

265 and  $VAC_{Na}$  should be attributed to the good ions transfer channel of MG-1.6 resulting from the large  
 266 fraction of mesopores.  $GAC_{Na}$  and deionization rate can be facilitated by favorable pore size  
 267 distribution. Mesopore is very beneficial to decrease transfer resistance and provides superior ions  
 268 transfer channel, so that the consumed ions can be replenished quickly from bulk solution, thus very  
 269 favorable for enhancing deionization capacity. To compared with some reported literatures in the same  
 270 calculation method, a batch-mode CDI test using the AC || MG-1.6 electrode pairs were carried out  
 271 (Figure S7a and S7b). The calculation methods of  $VAC_{NaCl}$  and  $GAC_{NaCl}$  have taken into account the  
 272 effect of current collectors and both the cathode and anode electrode materials mass. The  $VAC_{NaCl}$  and  
 273  $GAC_{NaCl}$  were calculated to  $14.3 \text{ mg/cm}^3$  and  $19.4 \text{ mg/g}$ , respectively. Compared to the reported  
 274 literatures, the  $VAC_{NaCl}$  reaches high level and  $GAC_{NaCl}$  is also slightly superior (Figure 4d and S7c,  
 275 Table 1 and S2).<sup>25,47-55</sup> The  $GAC_{Na}$  and  $ASAR_{Na}$  at different flow rates were studied (Figure S8b and  
 276 S8c) and the results show negligible difference among the applied flow rates, implying no obvious  
 277 impact on  $GAC_{Na}$  and  $ASAR_{Na}$  and exhibits good stability under different flow rates. Performance of  
 278 MG-1.6 at different direct voltages was investigated (Figure S9a, S9b and S9c) and a high  $VAC_{Na}$  was  
 279 acquired at 1.2 V. The effect of the initial concentration of NaCl solution on  $GAC_{Na}$ ,  $VAC_{Na}$ , and  
 280  $ASAR_{Na}$  was studied (Figure S10a, S10b and S10c) and the result shows that both  $GAC_{Na}$  and  $VAC_{Na}$   
 281 increases with the rising initial concentration. The pH value change was investigated during the  
 282 desalination and regeneration (Figure S11a and S11b). The change of pH may be due to the  
 283 decomposition of local water.<sup>56</sup> MG-1.6 also display good performance to remove the heavy metal ions.  
 284 At low concentration of  $0.31 \text{ mmol/L Cu}^{2+}$  aqueous solution, the removal rate of  $Cu^{2+}$  by MG-1.6  
 285 reached to 92.3% (Figure S12a). While, at low concentration of  $0.48 \text{ mmol/L Pb}^{2+}$  aqueous solution,  
 286 the removal rate of  $Pb^{2+}$  by MG-1.6 reached to 91.3% (Figure S12b). A good regeneration ability of

MG-1.6 was examined in 100 mg/L NaCl aqueous solution at 1.2 V and 60 mL/min and showed good regeneration stability up to 50 CDI cycles (Figure S13). These results are because of good chemical stability and capacitor characteristics of MG-1.6.

*In-situ* Raman spectra were conducted for exploring the mechanism of Na-ions storage of MoS<sub>2</sub> (Figure S14). The results show the ratio of characteristic peaks, E<sub>2g</sub><sup>1</sup>/A<sub>1g</sub>, of 2H MoS<sub>2</sub> decreased with potential decrease from 0 V to -0.5 V at the start stage and increase during the potential increased from -0.5 V to 0.5 V, then decrease during the potential decrease from 0.5 V to 0 V at the end of the whole CV cycle (Figure 5a, Table S3). This result is related with Na<sup>+</sup> insertion reaction in the interlayers of MoS<sub>2</sub> as follow.



Because Raman peak A<sub>1g</sub> is sensitive to interlayer electron density. The binding to electrons during the faradaic reaction (13) lead to increasing the interlayer electron density of MoS<sub>2</sub>, resulting in a decrease in A<sub>1g</sub> strength and an increase in E<sub>2g</sub><sup>1</sup>/A<sub>1g</sub>.<sup>57,58</sup>

In order to more clearly prove the phase transformation from 2H MoS<sub>2</sub> to 1T MoS<sub>2</sub>, HAADF-STEM was conducted to observe the atom array. A mixed phase in the area was founded indicating the co-existence of 2H and 1T MoS<sub>2</sub> after 50 CDI cycles (Figure 5c). Before CDI cycles of the regeneration test, the as-prepared electrode was characterized by Raman spectra and no peaks of 1T MoS<sub>2</sub> was found (Figure 5b). However, after 50 CDI cycles, the characteristic peaks of 1T MoS<sub>2</sub> were found at 150 and 233 cm<sup>-1</sup> corresponding to the known J1 and J2 peaks.<sup>59-61</sup> Therefore, an inference that the 2H MoS<sub>2</sub> partly transferred to 1T MoS<sub>2</sub> is reasonable (Figure 5d). For NaCl removal using AC || MG-1.6 electrode pairs, the whole deionization process is described below. Firstly, Na<sup>+</sup> migrates to polarized cathode under electrostatic force and adsorbed on the surface of the electrode. Then, some Na<sup>+</sup> ions

were embedded in the interlayer of MoS<sub>2</sub>, and Faradaic reaction (13) occurs and MoS<sub>2</sub> changed from 2H phase to 1T phase. Simultaneously, Cl<sup>-</sup> ions were adsorbed into the electrical double layers between the carbon surface and the bulk NaCl solution. The final material saturates sodium. In the regeneration stage, Na<sup>+</sup> and Cl<sup>-</sup> ions adsorbed in the surface electric double-layer are first released. Then, the Na<sup>+</sup> ions embedded in the MoS<sub>2</sub> layer reacts (14) inversely, and some MoS<sub>2</sub> transforms into 2H phase, while others remain 1T phase. As for the reasons of partial phase transition, more in-depth study is needed. For CDI, we first use HAADF-STEM to study the phase composition in hybrid MoS<sub>2</sub>-graphene CDI electrodes. The high VAC<sub>NaCl</sub> electrodes prepared in this study present a promising approach to miniaturizing CDI devices for future applications.

## ■ ASSOCIATED CONTENT

### Supporting information

Non-active materials deionization plots, TEM images, thickness of T<sub>t</sub> and T<sub>cc</sub>, dynamic water contact angle analysis. GCD, CV curves, IR drop and capacitance of different samples. Plots of GAC<sub>NaCl</sub>, VAC<sub>NaCl</sub> and NSC *vs.* time for MG-1.6 using AC || MG-1.6 electrode pairs. Plots of NSC *vs.* time for different samples with graphite film as counter electrodes. Plots of NSC, VAC<sub>Na</sub>, GAC<sub>Na</sub> *vs.* time for MG-1.6 using GF || MG-1.6 electrode pairs under different condition. Plots of removal of heavy metal ions, NSC and pH *vs.* time, regeneration plots using GF || MG-1.6 electrode pairs. *In-situ* Raman spectra of a CV cycle, comparison of MoS<sub>2</sub>-graphene hybrid electrodes and AC electrodes, comparison tables of AC electrode, peaks ratio, reported materials and this work.

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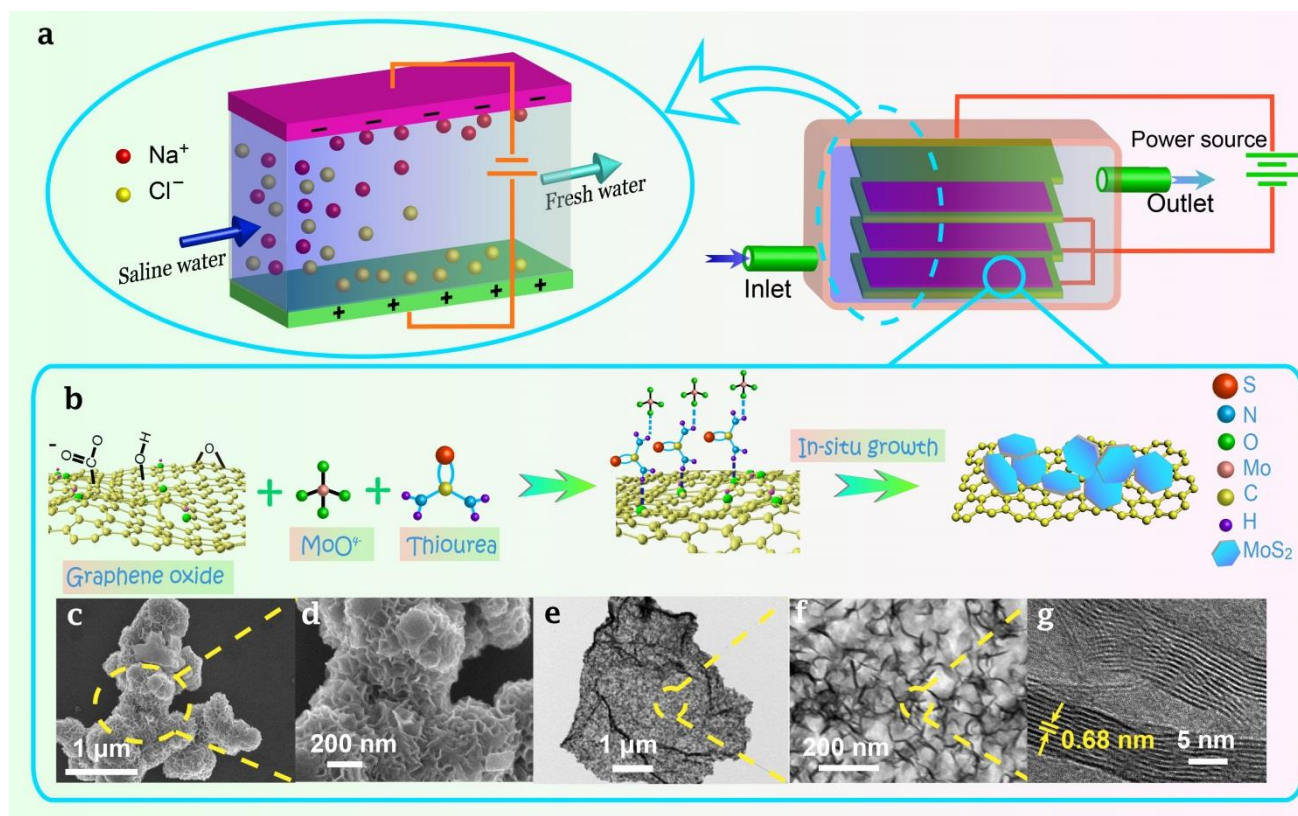
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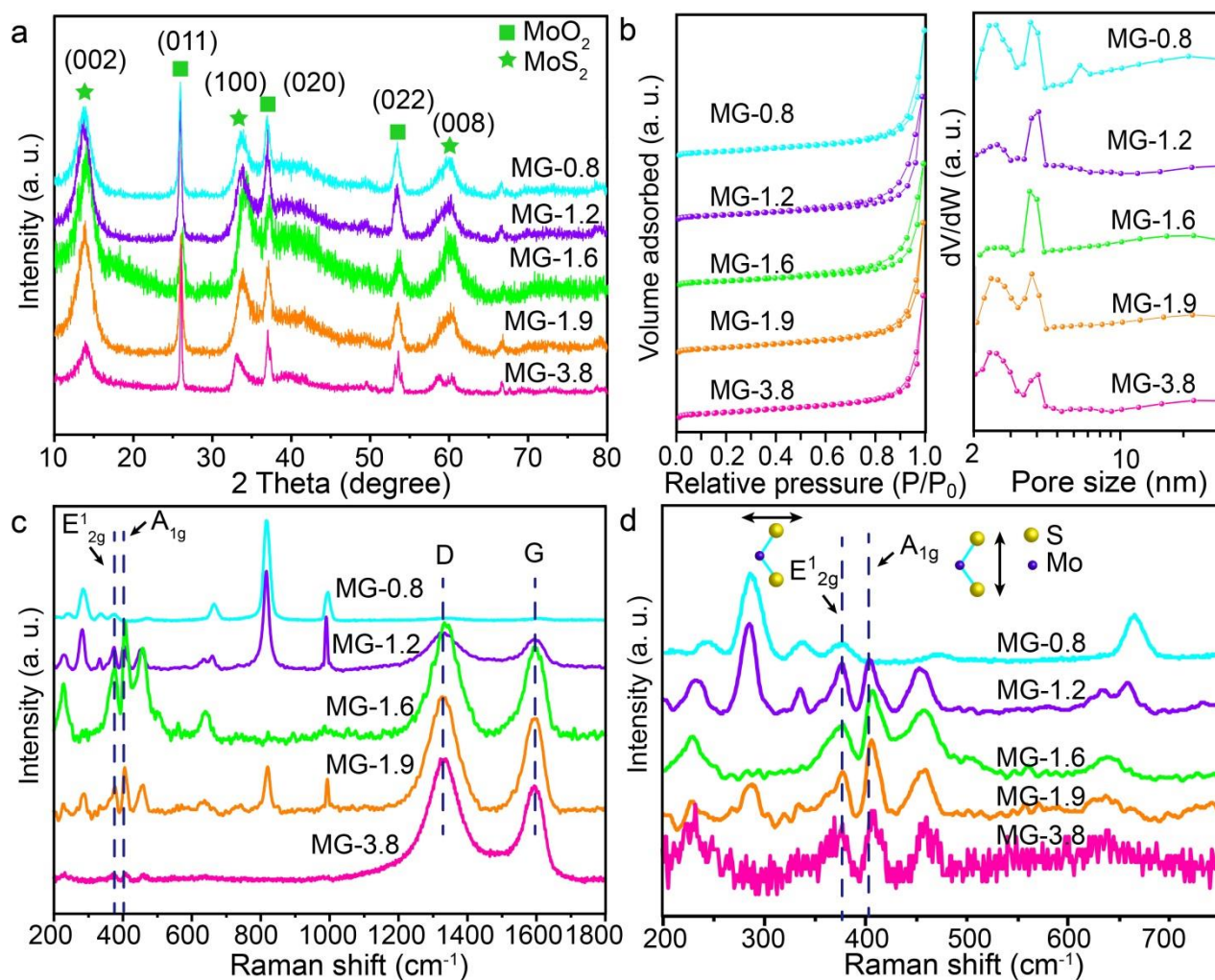
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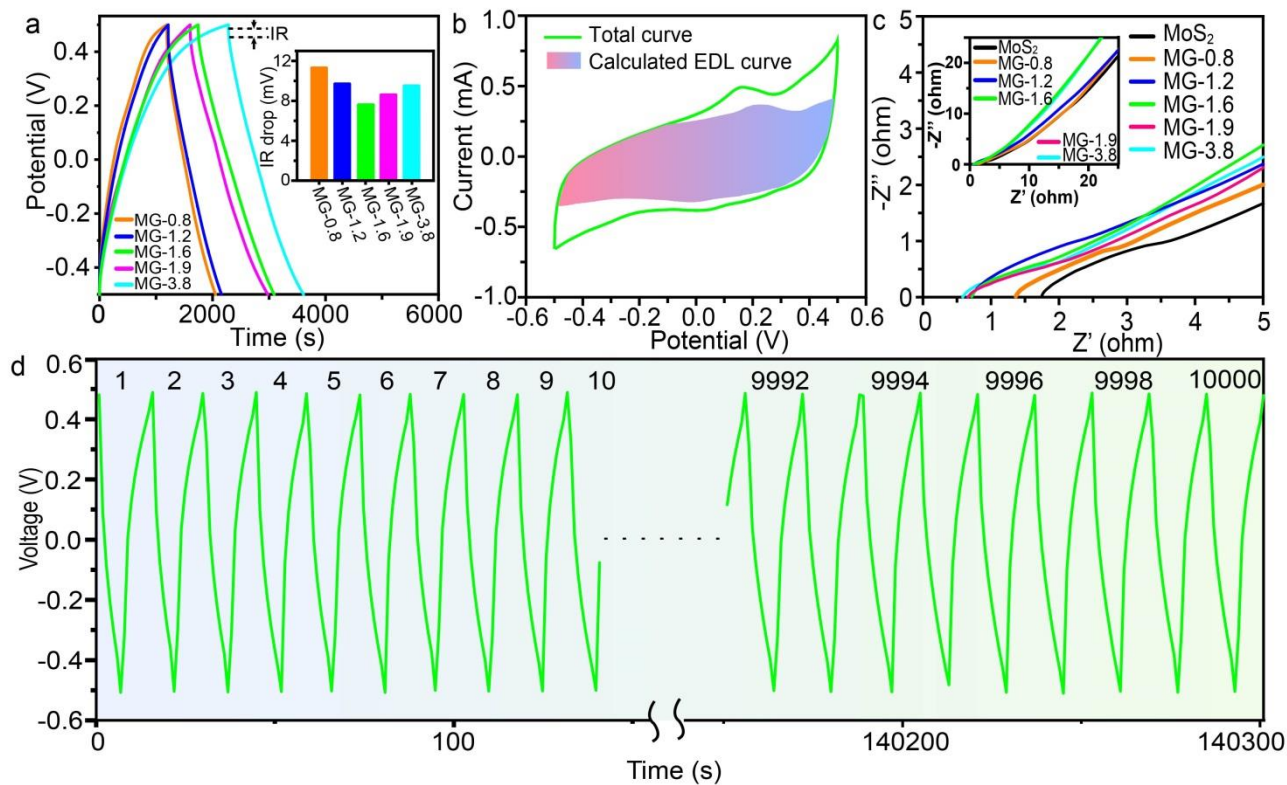




**Figure 1.** (a) Schematic illustration of CDI device; (b) Schematic illustration of preparation of  $\text{MoS}_2$ -graphene hybrids; (c and d) SEM images of MG-1.6; (e and f) TEM images of MG-1.6; (g) HRTEM image of MG-1.6.

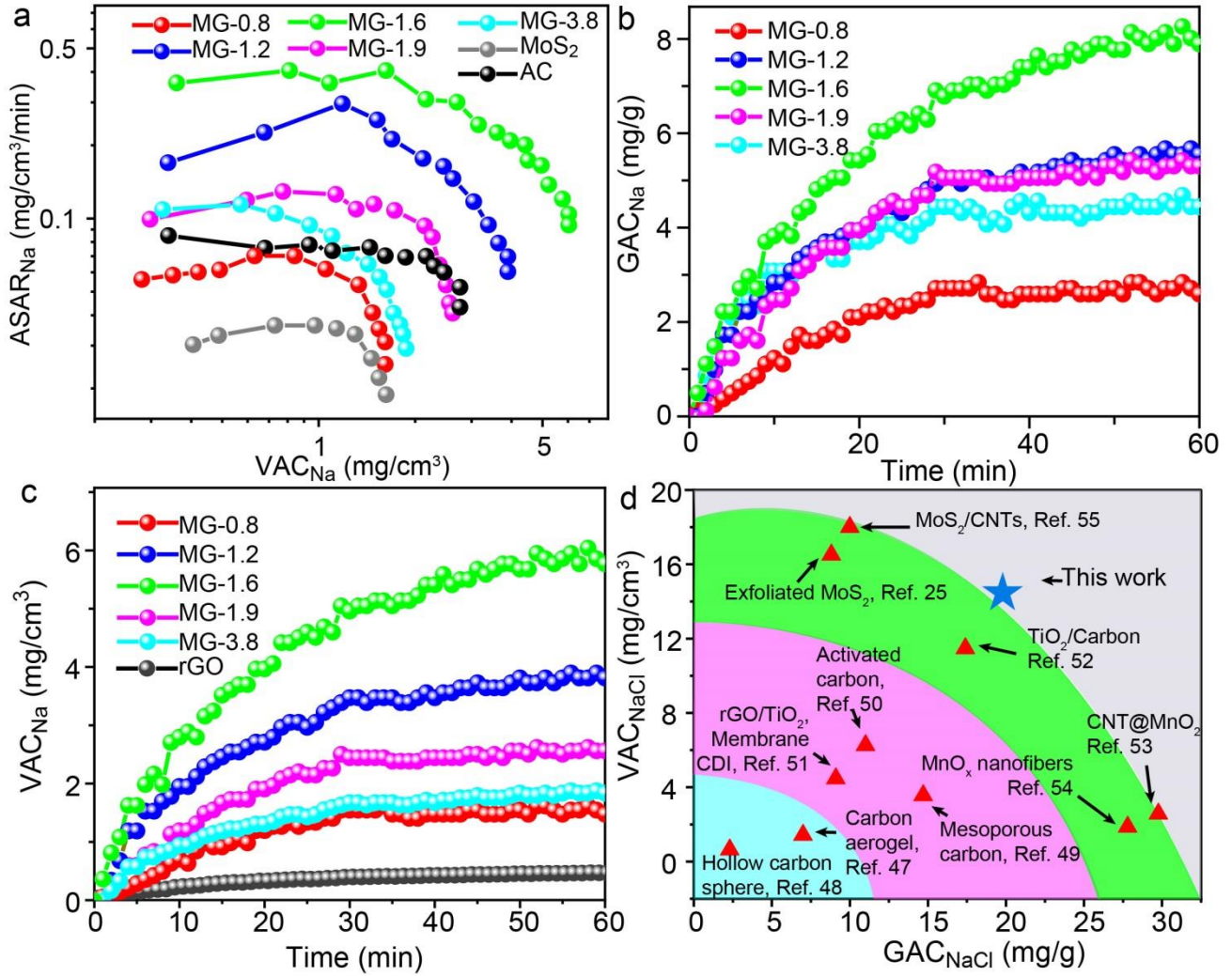


**Figure 2.** (a) XRD patterns, (b) N<sub>2</sub> adsorption-desorption isotherms (left) and BJH pore size distribution profiles (right), (c) full Raman spectra and (d) local-magnified Raman spectra of different samples.

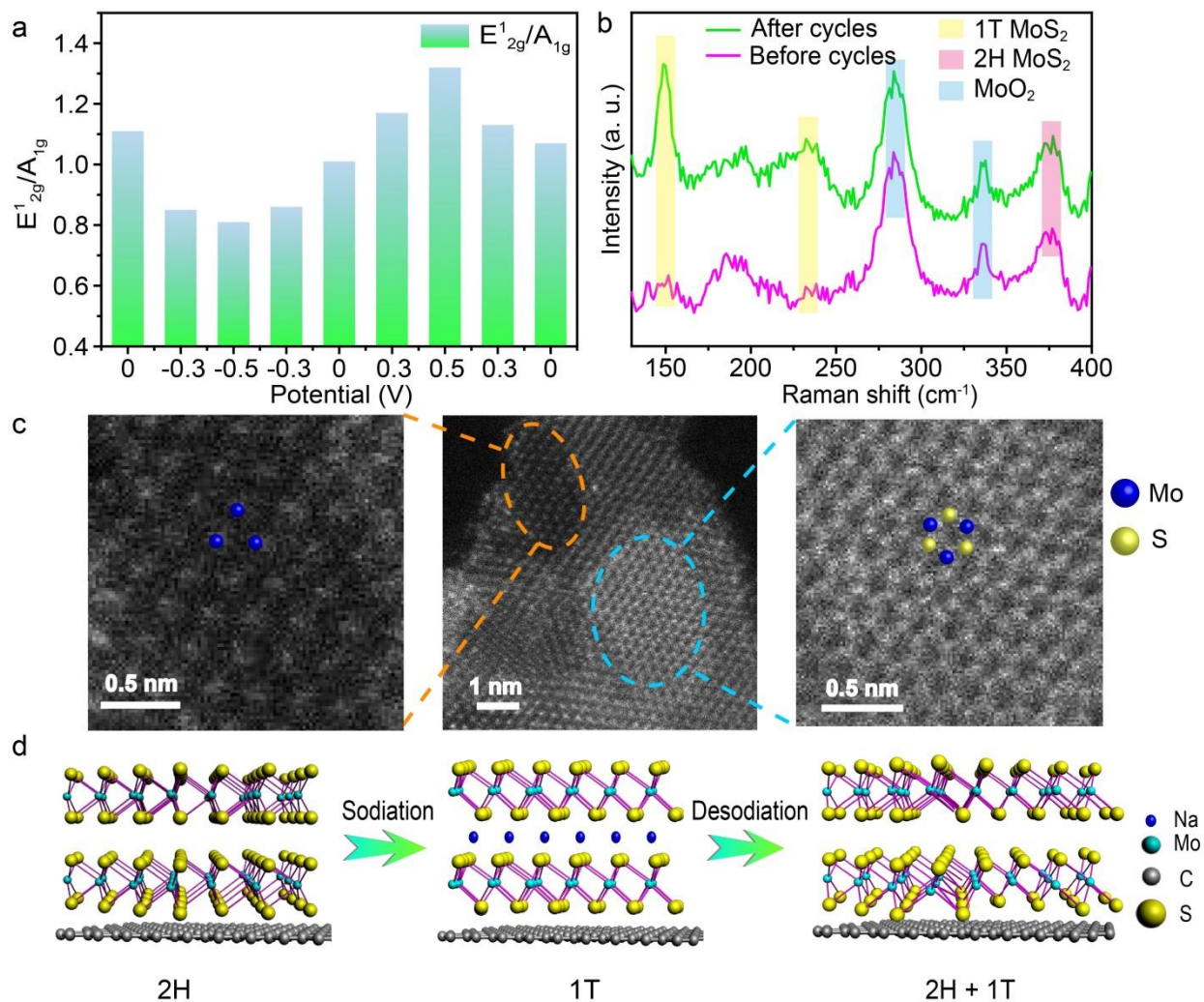


**Figure 3.** (a) GCD curves at a current density of 0.2 A/g (the inset is IR drop of different samples); (b) CV curves at a scanning rate of 0.2 mV/s (the shadow is the calculated capacitive charge); (c) EIS curves of different samples (the inset is the full EIS); and (d) Long GCD cycles of MG-1.6 at a current density of 5 A/g.





**Figure 4.** (a) Ragone curves of different samples in a 500 mg/L NaCl aqueous solution at 1.2 V and 60 mL/min; (b) Plots of GAC<sub>Na</sub> vs. deionization time of different samples in a 500 mg/L NaCl aqueous solution at 1.2 V and 60 mL/min; (c) Plots of VAC<sub>Na</sub> vs. deionization time of different samples in a 500 mg/L NaCl aqueous solution at 1.2 V and 60 mL/min; and (d) Comparison of VAC<sub>NaCl</sub> and GAC<sub>NaCl</sub> between the reported materials and material of this work.



**Figure 5.** (a) *In-situ* Raman spectra peak ratio of  $E^{1}_{2g}/A_{1g}$  of MG-1.6 during a CV cycle range from -0.5 V to 0.5 V ;  
 (b) Raman spectra of MG-1.6 before and after 50 cycles; (c) HAADF-STEM images of MG-1.6 after 50 CDI cycles  
 (the left image corresponding to 1T  $\text{MoS}_2$ , the right image corresponding to 2H  $\text{MoS}_2$ ); and (d) Schematic illustration  
 of sodiation and desodiation of 2H  $\text{MoS}_2$ .

**Table 1.** Comparison of between reported CDI electrodes and this work.

Materials	GAC <sub>NaCl</sub> (mg/g)	VAC <sub>NaCl</sub> (mg/cm <sup>3</sup> )	Reference
MoS <sub>2</sub> -graphene	19.4	14.3	This work
Carbon aerogel	~7	1.43	47
Hollow Carbon sphere	2.3	0.64	48
Mesoporous carbon	14.7	3.56	49
Activated carbon	11	6.26	50
reduced GO/TiO <sub>2</sub>	9.1	4.47	51
TiO <sub>2</sub> /Carbon	17.4	11.47	52
Carbon nanotube@MnO <sub>2</sub>	29.77	2.57	53
MnO <sub>x</sub> nanofiber	27.8	1.87	54
MoS <sub>2</sub> /Carbon nanotube	10	18	55
Exfoliated MoS <sub>2</sub>	8.81	16.51	25

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TOC

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